

KOKAI PATENT APPLICATION NO. 2003-94414

**AMORPHOUS CERAMIC FABRICATION METHOD**

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AMORPHOUS CERAMIC FABRICATION METHOD

[*Amorufasu seramikkusuno seikeihoh*]

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## Specification

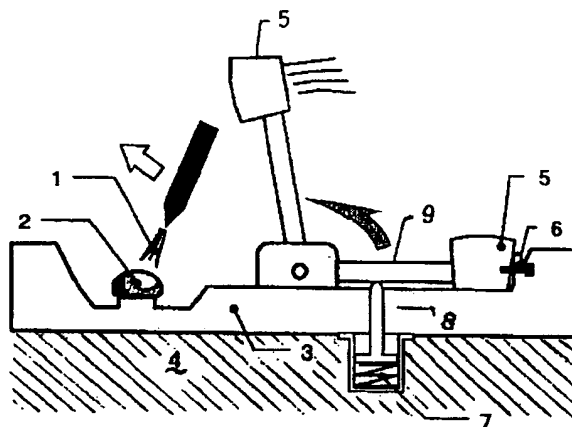
## [Title of the invention]

## Amorphous ceramic fabrication method

## [Abstract]

[Purpose] The purpose of the present invention is to provide a method for plastic working of amorphous ceramics at temperatures in a range that is industrially feasible.

[Means of solution] A raw material melt is formed comprising a powder or compact of a ceramic made of Ln (Ln is at least one type of rare earth metal element), A (A is one or more elements selected from the group consisting of Al, Cr, Fe and Ga) and O, the melt (oxide) is super-quenched or vapor phase deposited to form an amorphous material, the amorphous material is inserted into a die press and plastic working is done under a supercooled liquid state in the region between the transition temperature and the crystallization temperature of the aforementioned material.



## [Claim of the invention]

[Claim 1] A method for fabrication of amorphous ceramics characterized by the fact that a melt is formed for a raw material comprising a powder or compact of ceramics made of Ln (Ln is at least one type of rare earth metal element), A (A is one or more elements selected from the

group consisting of Al, Cr, Fe and Ga) and O, the melt (oxide) is super-quenched or vapor phase deposited to form an amorphous material, the amorphous material is inserted to a die press and plastic working is done under a supercooled liquid state in the region between the transition temperature and the crystallization temperature of the aforementioned material.

[Detailed description of the invention]

[0001]

[Technical field of the invention] The present invention pertains to a method for fabrication of amorphous ceramics having high heat resistance and abrasion resistance.

[0002]

[Prior art] In the past, as a method for production of ceramic components with a specific shape, a method where a powder is sintered and a method where a solid material is machined have been used, but the sintering method has technical problems associated with it such as estimation of the dimensions after sintering, and a machining process accompanies fabrication. As a means to eliminate the aforementioned problems, plastic working of a ceramic that utilizes the super-plastic phenomenon that occurs in a high temperature environment is being examined, but remains in the research stage.

[0003]

[Problems to be solved by the invention] The mechanism of super-plastic phenomenon is based on rotation of individual crystal particles that comprise the material and in order to achieve this, a very high temperature is required and furthermore, it is necessary to use a very fine raw material powder, which makes industrial application difficult. On the other hand, product cost increases when machining is done. The higher the heat resistance, abrasion resistance, and strength of the ceramic to be processed, the greater the difficulty, and broader use of high performance ceramics is blocked. The present invention is based on the above background, and the purpose of the present invention is to provide a method for plastic working of amorphous ceramics in a temperature range that is industrially feasible.

[0004]

[Means to solve the problem] In a part of the material formed into an amorphous melt, transition occurs in a supercooled liquid that is peculiar to the material. In the fabrication method of the present invention, a ceramic having a specific composition is formed into an amorphous melt, and fabrication of the material is done at the transition temperature range of a supercooled liquid.

In other words, the present invention is a method for fabrication of amorphous ceramics characterized by the fact that a melt is formed for a raw material comprising a powder or compact of a ceramic made of Ln (Ln is at least one type of rare earth metal element), A (A is one or more elements selected from the group consisting of Al, Cr, Fe and Ga) and O, the melt (oxide) is super-quenched or vapor phase deposited to form an amorphous material, the amorphous material is inserted to a die press and plastic working is done under a supercooled liquid state in the region between the transition temperature and the crystallization temperature of the aforementioned material.

[0005] Forming of the ceramic amorphous material is not especially limited, and super-quenching where a ceramic having a specific composition is super-quenched (aforementioned Ln-A-O), vapor phase deposition, etc. can be mentioned. When fabrication is done in the supercooled liquid temperature range using an amorphous material formed into a powder or a mixture of an amorphous material and crystals as a raw material, production of a bulk compact with high-density can be done at a temperature significantly lower than that of conventional hot super-plastic fabrication processes and a reduction in fabrication cost can be expected. In this case, "amorphous" means an atomic structure with a crystal lattice cannot be observed when examined by a transmission electron microscope, and "crystalline" means an atomic structure with a crystal lattice can be observed when examined by a transmission electron microscope.

[0006]

[Embodiment of the invention] The ceramic raw material used in the present invention is an Ln-A-O composition. For Ln, one or more rare earth metals selected among the group consisting of

Er, Yb, Dy, Y, Gd, La, Sm, Ce, Pr, Nd, Eu, Tb, Ho, Tm and Lu, and from the standpoint of high stability of the resulting amorphous ceramic supercooled liquid, Gd and La are especially desirable. For A, one or more elements selected from the group consisting of Al, Cr, Fe, and Ga can be mentioned.

[0007] A suitable content of Ln, A and O varies depending on the combination of Ln and A, and approximately,  $\pm 10$  wt% of the eutectic point composition for each composition is suitable. The composition is specified within the above-mentioned range since the farther the composition is from the eutectic point composition, the narrower the transition temperature range, and fabrication while maintaining the supercooled liquid state becomes difficult in compositions of beyond  $\pm 10$  wt%.

[0008] In general, oxides of Ln and oxides of A are used for the aforementioned raw materials, and those that form oxides upon melting, for example, hydroxides, carbonates, etc. may be used as well. For the form of the raw material used, either a powder, compact, sinter, or solid material may be used, and furthermore, a combination of two or more of the same may be used as well.

[0009] The melting method for the aforementioned raw material is not especially limited as long as a method capable of heating to the melting point of the raw material is used, and for example, arc, laser electron beam, light, infrared, high frequency waves, etc. may be used as the heat source. When high frequency waves are used, it is necessary to place the aforementioned material in a crucible (container) having conductivity and a melting point higher than the melting point of the raw material since the raw material exhibits hardly any conductivity at or near room temperature. For example, a crucible made of Mo, W, Ta, Ir, Nb, etc. can be used effectively. Furthermore, when the raw material is a powder, a crucible made of the aforementioned materials and a container comprising a crucible and a support are required, and in this case, in addition to the aforementioned crucible, a container comprising a crucible and a support made of Cu chilled with water, etc. may be used as well. The aforementioned crucibles and containers can be used effectively when the raw material is not a powder as well.

[0010] Melting of the materials may be done under atmospheric air, inert gas, reducing gas, hydrocarbon gas, vacuum, etc., and when a container that is likely to be oxidized under a high temperature atmosphere is used, it is desirable when melting is done in an inert gas atmosphere such as argon gas and helium gas or in a vacuum. Furthermore, when melting of the raw materials is done by an arc, it is necessary for sufficient argon gas for generation of the arc to be included in the atmosphere.

[0011] The method used for forming the molten oxide into an amorphous material is not especially limited, and a single roll method, double roll method, rapid cooling method such as the Hammer-Albin method, fiberization method such as melt-extraction, a vapor deposition method such as sputtering, etc. can be mentioned.

[0012] For fabrication of the amorphous ceramic raw material produced as described above, the raw material is inserted to die press and heated and pressure is applied to the die press at a temperature between the transition temperature ( $T_g$ ) and the crystallization temperature ( $T_x$ ) with the material under in a supercooled liquid state. Measurement of the transition temperature and crystallization temperature is done by a differential scanning calorimeter (DSC). Upon measuring the temperature at the time of fabrication, it is desirable when the temperature of the fabrication raw material is measured directly since a temperature difference exists between the die temperature and the fabrication material, and fabrication upon estimating the raw material temperature based on an appropriate adjustment may be possible. For the fabrication method, in addition to press fabrication, compression, rolling, extrusion, drawing, casting, deep drawing, etc. may be used.

[0013] The aforementioned fabrication may be done under atmospheric air, inert gas, reducing gas, hydrocarbon gas, vacuum, etc., and when a press die that is likely to be oxidized under a high temperature atmosphere, it is desirable when the fabrication is done in an inert gas atmosphere such as argon gas or helium gas or in a vacuum. Furthermore, for reduction of residual air bubbles inside the raw material and compact, it is desirable when the fabrication is



done in a vacuum.

[0014] Some raw material components have multiple crystallization temperatures as a result of stepwise crystallization from the amorphous phase, and from the standpoint of flow properties of the supercooled liquid, fabrication at a temperature below the crystallization temperature on the minimum temperature side. Depending on the intended application after fabrication, it is possible to select an appropriate fabrication temperature to promote partial crystallization. After fabrication, an appropriate heat treatment is provided to form a complete or partial crystallization to produce compacts with many different properties.

[0015]

[Working Examples] The present invention is explained further in specific terms with working examples and comparative examples below.

[Working Example 1]

As a raw material,  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and  $\text{Gd}_2\text{O}_3$  powder were used. 77.5 moles of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and 22.5 moles of  $\text{Gd}_2\text{O}_3$  powder were added to ethanol, mixing was done by a ball mill, and natural drying was done to evaporate the ethanol from the resulting slurry to produce a mixed powder block. An arc was applied to the mixed powder block obtained to produce a button-like compact. Further arc melting was done for the button-like compact, and impact with a copper hammer and rapid cooling were provided by the cooling system shown in Fig. 1.

[0016] In the cooling system shown in Fig. 1, 3 is a copper hearth chilled with cooling water, copper hammer locked by latch pin 6 is supported so that it is free to rotate on aforementioned hearth 4, rod 8 that is forced out based on the operation of spring 7 impacts hammer handle 9 causing it to rotate, the hammer head 5 impacts sample 2 and rapid cooling of sample is achieved.

[0017] As a result of rapid cooling achieved by the above-mentioned device, a compact mixed with an opaque portion and transparent portion is produced. When examined by a microscope, crystal particles are observed in the opaque portion and the opacity appears to be caused by

irregular reflection of light at the boundary of the crystal particles. When the transparent portion of the compact was removed, and measurements were made by powder X-ray analysis, a halo pattern was observed, and it was further confirmed that the aforementioned portion is an amorphous phase. Furthermore, according to the DSC analysis, heat generation that accompanies crystallization was observed at 1210K and 1288K and the endothermic change accompanies transition to a supercooled liquid was observed at a temperature in the range of 1149K to 1196K as shown in Fig. 2.

[0018] The amorphous piece obtained upon rapid cooling was pulverized to form a powder and poured into a press die made of graphite having a cylindrical sample chamber with an inner diameter of 9 mm and height of approximately 15 mm, a vacuum atmosphere was achieved at a specific pressure (60 MPa) and the temperature was increased to a specific temperature (1203K). Based on the temperature record and dislocation at the time of fabrication shown in Fig. 3, a sudden shrinkage was observed at the supercooled liquid transition temperature (876°C) measured by DSC. It is hypothesized that a sudden increase in density took place at the time of the transition of the raw material powder to a supercooled liquid state.

[0019] The cross-section of the compact removed is uniformly filled, and floating of polygonal crystal pieces inside a uniform structure was observed based on examination of the structure at a high magnification. The supercooled liquid state ceramic surrounds the pieces of crystal mixed in the raw material and high compactness is achieved. As described above, formation of a dense compact is made possible when a crystalline material is mixed with the raw material. The compact produced by the aforementioned method exhibits a compression strength of 1800 MPa and has the strength of ceramics produced by standard methods despite the low temperature fabrication used in this case.

[0020] [Working Example 2]

A mixed powder block of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and  $\text{Gd}_2\text{O}_3$  powder was produced as in the case of Working Example 1 above. An arc was applied to the aforementioned block to produce a

button-like compact. Further arc melting was done for the button-like compact, and production of a fibrous ceramic was achieved by a melt extrusion method where a rotating copper disc is brought into contact. The aforementioned fibrous ceramic was formed into an amorphous material as a result of rapid cooling, low temperature fabrication was applied to the crushed powder produced as in the case of Working Example 1.

[0021] [Working Example 3]

A mixed powder block of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and  $\text{Gd}_2\text{O}_3$  powder was produced as in the case of the aforementioned Working Example 1. An arc was applied to the aforementioned block to produce a button-like compact. Further arc melting was applied to the button-like compact under high-speed rotation, and an amorphous ceramic chip was produced by a rapid cooling plasma rotary electrode powder formation machine where flying ceramic droplets are quenched by a cooling plate. The aforementioned amorphous ceramic chip was crushed to form a powder and low-temperature fabrication was done for the crushed powder as in the case of Working Example 1.

[0022] [Working Example 4]

As a raw material,  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and  $\text{Gd}_2\text{O}_3$  powder were used, and for a mixed powder of 77.5 moles of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and 22.5 moles of  $\text{Gd}_2\text{O}_3$ , 1% (100 ppm molar ratio) of  $\text{SiO}_2$  powder was added and the material was formed into an amorphous material as in Working Example 1. The resulting amorphous ceramic exhibited a crystallization behavior similar to the case where  $\text{SiO}_2$  was not added. Furthermore, when fabrication of the crushed amorphous powder was done according to the method described in Working Example 1, production of a compact with a high density was possible.

[0023] [Comparative example]

As a raw material,  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and  $\text{Gd}_2\text{O}_3$  powder were used. 77.5 moles of  $\alpha$ - $\text{Al}_2\text{O}_3$  powder and 22.5 moles of  $\text{Gd}_2\text{O}_3$  powder were added to ethanol, mixing was done by a ball mill, and natural drying was done to evaporate the ethanol from the resulting slurry to produce a

mixed powder. The mixed powder was formed into a disc with a diameter of 9 mm and thickness of 2 mm in an inert atmosphere at 1923°K x 2 hours using a hot press. The cross-section of the compact had a structure where fine  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles and Gd<sub>2</sub>O<sub>3</sub> particles were aggregated. Furthermore, bonding among the particles was insufficient and detachment of the particles at the time of polishing of the cross-section was observed. In this case, high temperature fabrication is necessary to produce a compact with the structure of the present invention based on the hot press method.

[0024]

[Effect of the invention]

Reduction of the cost of plastic working of ceramics is made possible when plastic working of a ceramic is done at a temperature in a range that is industrially feasible. In particular, a clear advantage can be achieved in fabrication of heat-resistant and abrasion-resistant ceramics and further use of ceramics can be promoted.

[Brief description of figures]

[Fig. 1] An example of the device used for rapid cooling achieved by impacting a molten ceramic with a copper hammer.

[Fig. 2] An example of DSC measurement of the amorphous ceramic produced in the present invention; heat generation that accompanies crystallization is observed at 1210K and 1288K and the endothermic change associated with transition to supercooled liquid is observed at a temperature in the range of 1149K to 1196K.

[Fig. 3] An example of temperature and dislocation record at the time of hot roll fabrication of an amorphous ceramic. Shifting toward plus side accompanies thermal expansion during temperature increase and a sudden shrinkage (shifting toward the negative side) occurs at temperatures in the range of the supercooled liquid state.

[Explanation of codes]

1: arc

2: sample

3: copper hearth

4: cooling water

5: copper hammer head

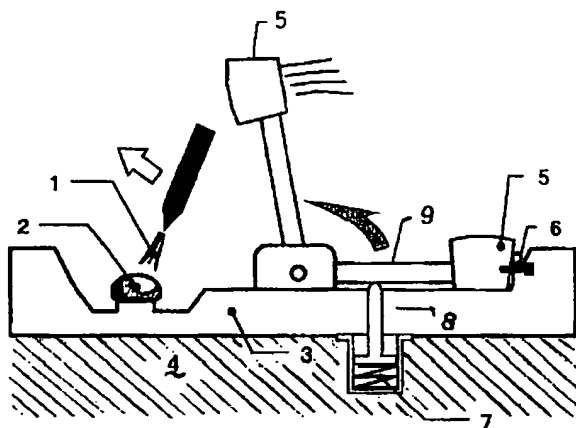
6: stopper pin

7: spring

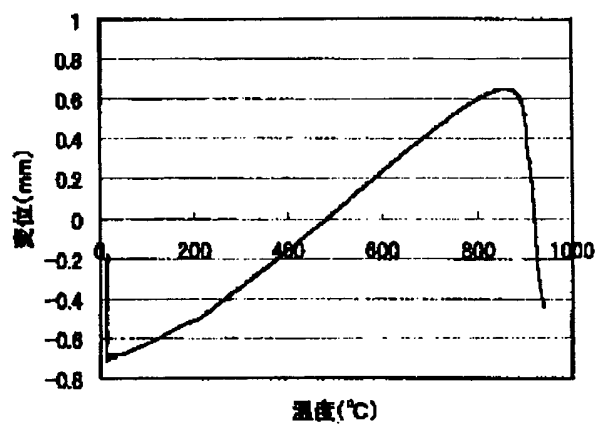
8: operation rod

9: hammer axis

[Fig. 1]



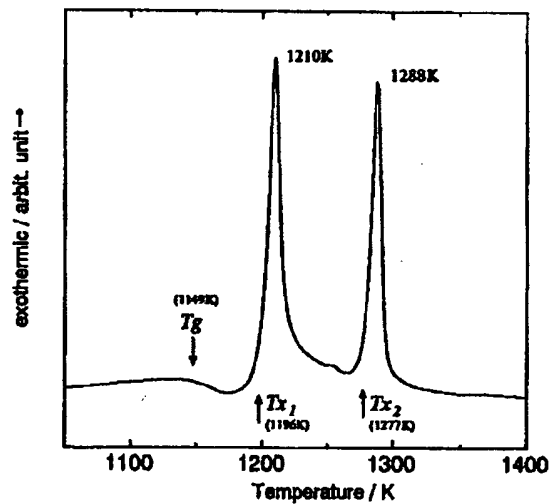
[Fig. 3]



Vertical axis: dislocation (mm)

Horizontal axis: temperature (°C)

[Fig. 2]



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